The limits of lithography and its relevance to nanotechnology (or: what will they build in our parking lot ?!)
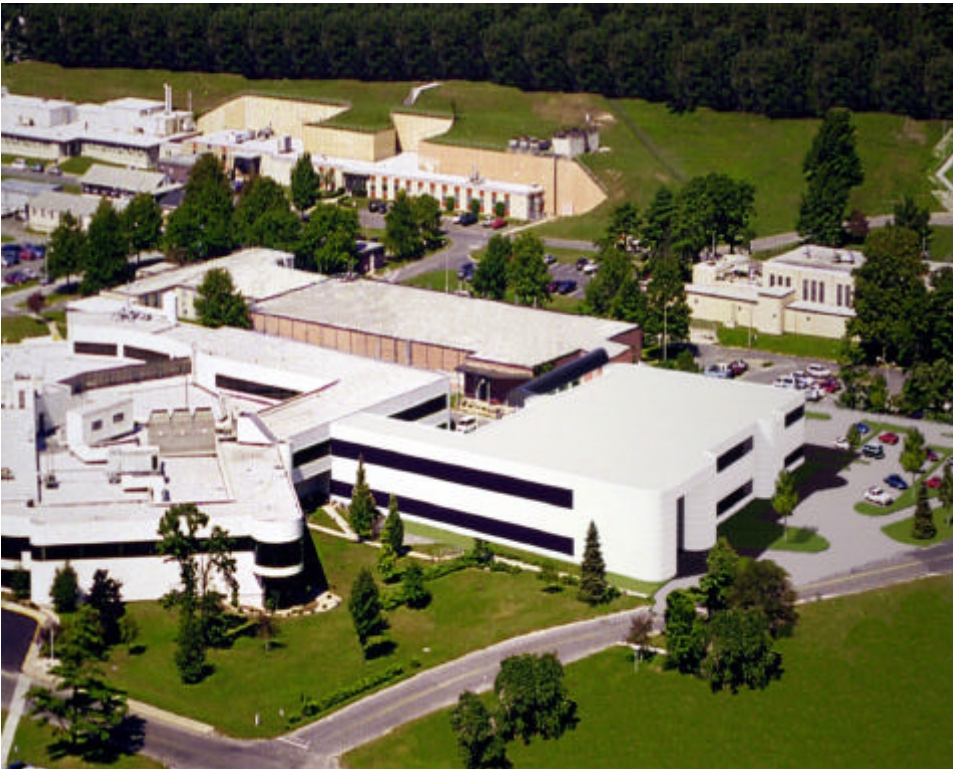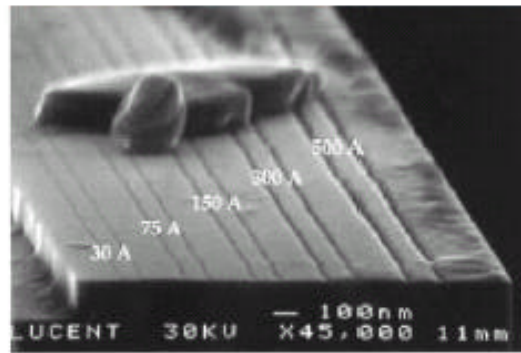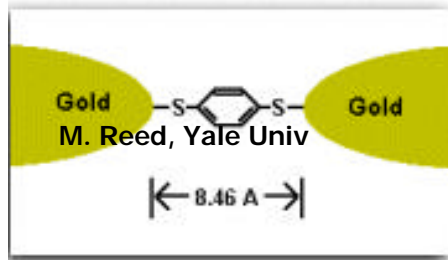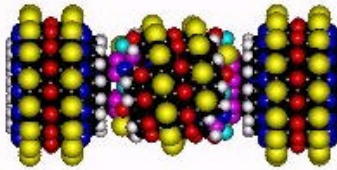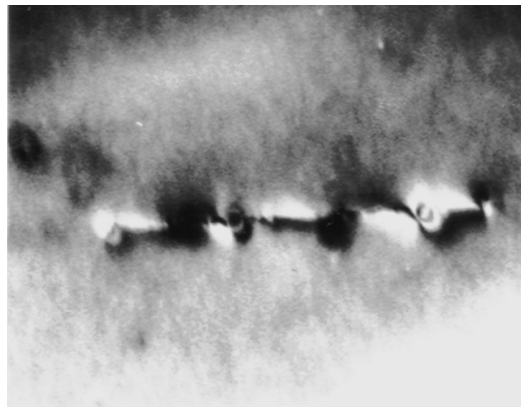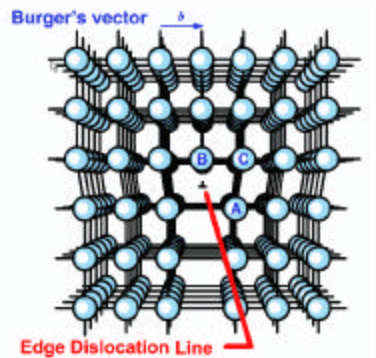John Warren
07/31/2002

- Clean rooms
- Vibration isolation of equipment
- Superior temperature, EMI isolation, and humidity control
- Common interaction areas
- Connected to NSLS and Instrumentation Division
- 78,500 sq. ft. lab and user space

What is Nanotechnology?

Gold —S— —S— Gold
M. Reed, Yale Univ
|← 8.46 A →|

LUCENT 30KU X45,000 11mm — 100nm

Substrate for Molecular Wires
(Stormer and Willet)

Burger's vector b
B C
A
Edge Dislocation Line

Ni precipitates on dislocation
in silicon (Warren)

Laboratory clusters

|	
Electron Microscopy	**High-resolution structural and chemical probes**
Materials Synthesis	**Bulk, thin film material synthesis capabilities**
Nanopatterning	**E-beam and Ion-beam writer, pattern transfer**
Scanning Probe Microscopy	**AFM, STM**
Ultrafast Short Wavelength Source	**Short wavelengh-short pulse lasers**
Nanocenter NSLS Beamlines	**Small angle X-ray scattering and microprobe**

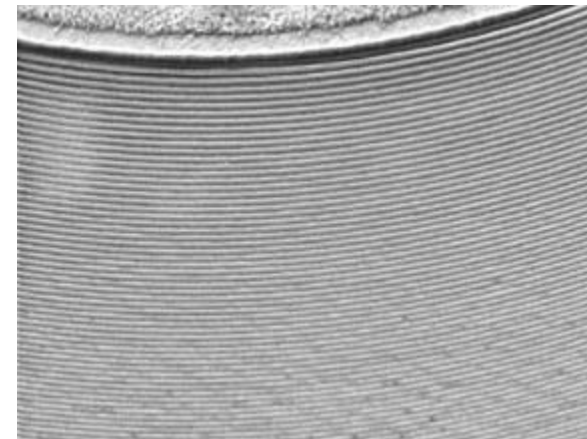# Nanopatterning Laboratory: Current Projects
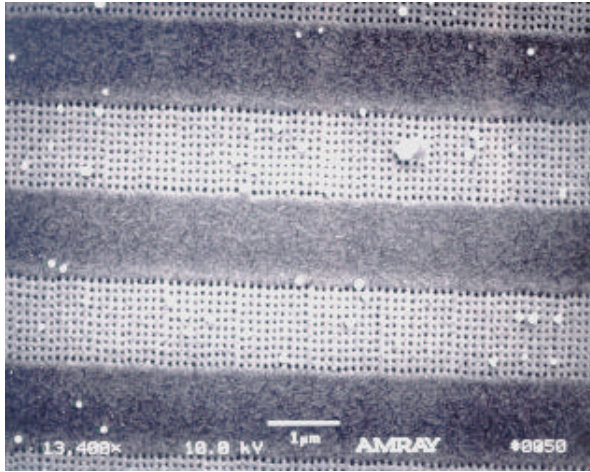
**Nanotemplate Directed Assembly of Soft Matter and Biomaterials**
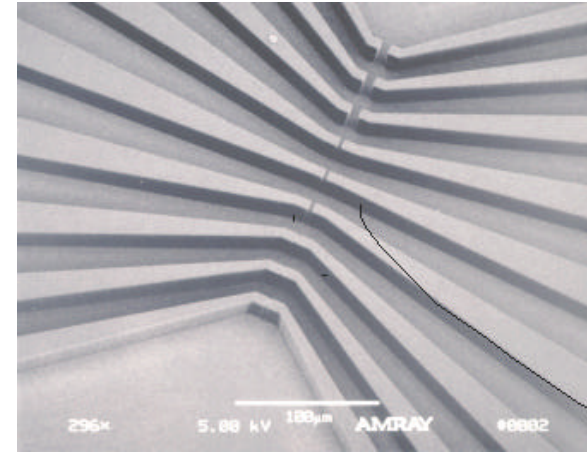
Charge injection and Transport in Nanoscale Materials: C. Creutz et al., Chemistry Dept., BNL
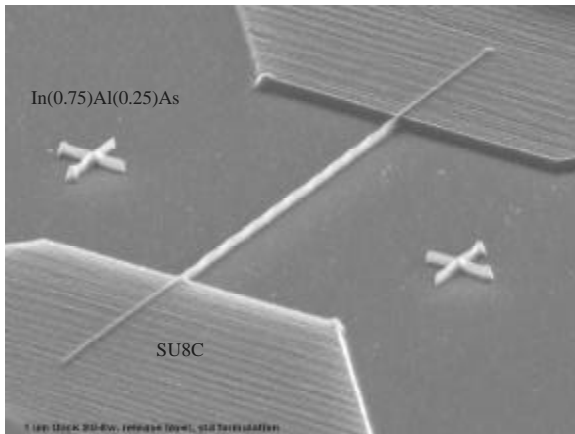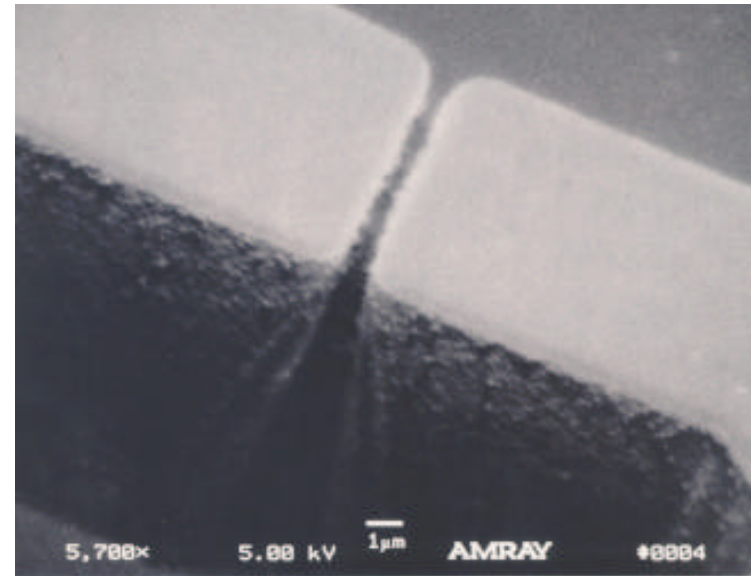

Hybrid Semiconductor-Superconductor Nanostructures: E. Mendez and F. Camino, Dept. of Physics and Astronomy, SUNYSB

Fresnel Zone Plate for X-Ray Microscopy at NSLS: C. Jacobson, Dept. of Physics and Astronomy, SUNYSB
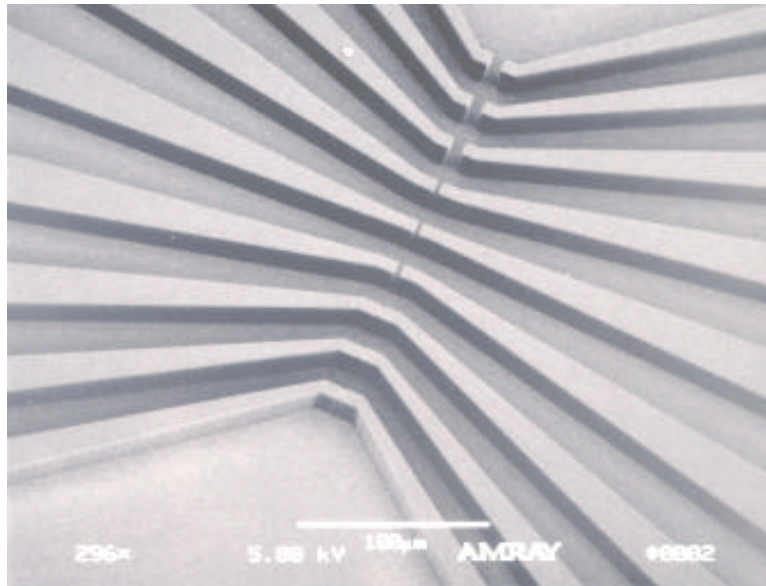
A

B

SEM micrographs of central gap in nanoelectrode microstructure. The nanoelectrode array (A) is composed of SU-8, a UV-sensitive negative resist. The electrodes are made conductive by using directional vacuum evaporation to coat the top surface of the electrode with a conducting Au/Cr layer. As shown in (B), metal is not deposited on the vertical sidewalls of the electrode, and electron isolation is maintained between the two halves of the electrode and the substrate.

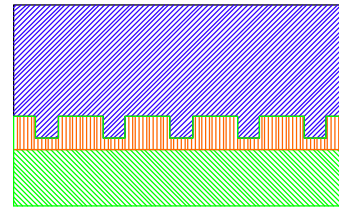# How will nanotechnology affect Instrumentation?
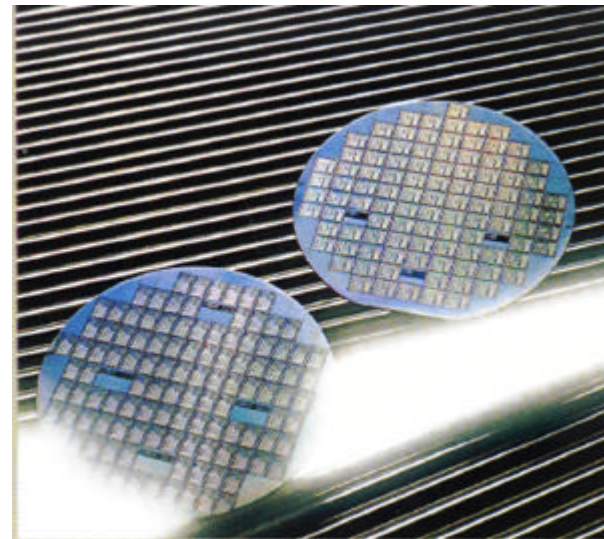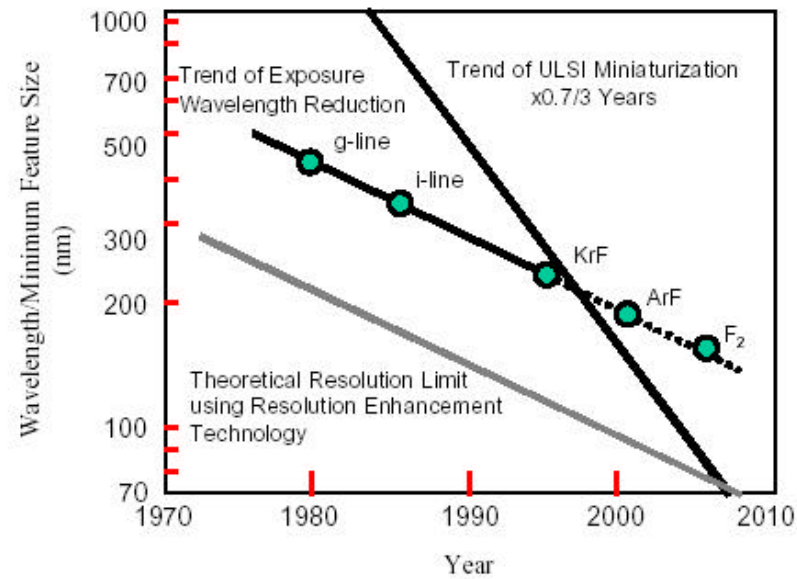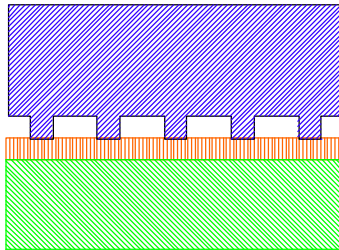
Nanoembossing: Is optical lithography obsolete?

mold in contact w. substrate
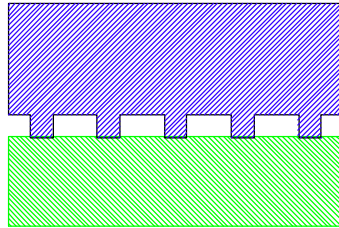
substrate melts < 250 ns

excimer laser radiation

substrate solidifies t > 250 ns
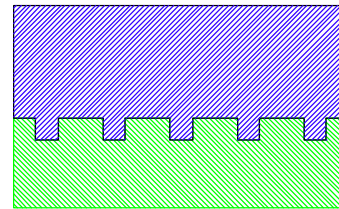
mold separated fm. substrate
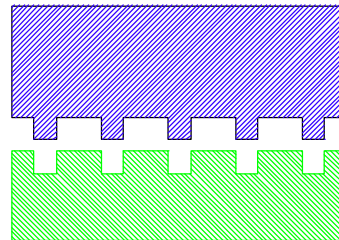
Ultrafast and direct imprint of nanostructures in silicon
S. Y.Chou C. Kelmel & J. Gu, Nature, vol. 417, 20 June 2002

Etched quartz embossing disc and silicon wafer after nanoembossing process:
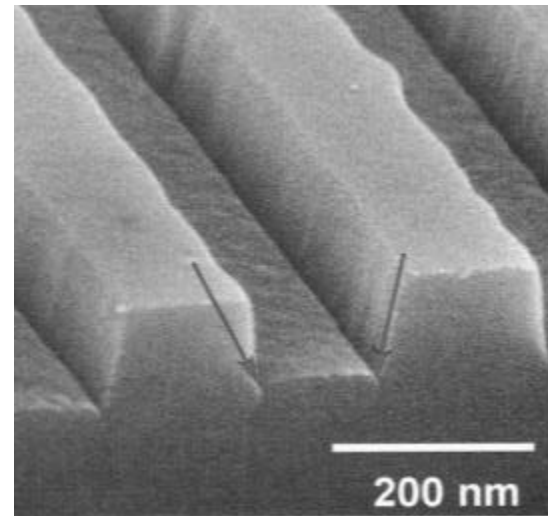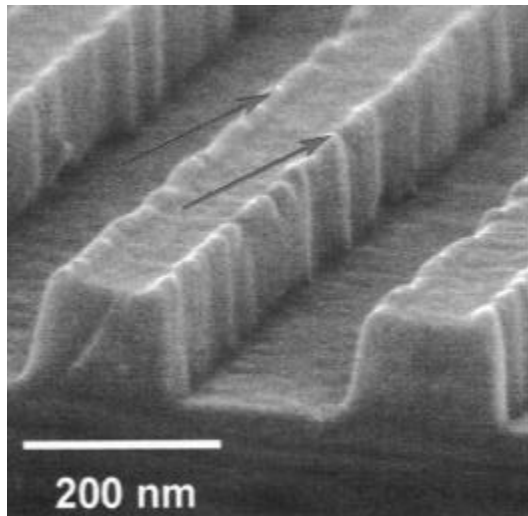
Ultrafast and direct imprint of nanostructures in silicon
S. Y.Chou C. Kelmel & J. Gu, nature, vol. 417, 20 June 2002

What is the distinction between direct-write and replication methods?
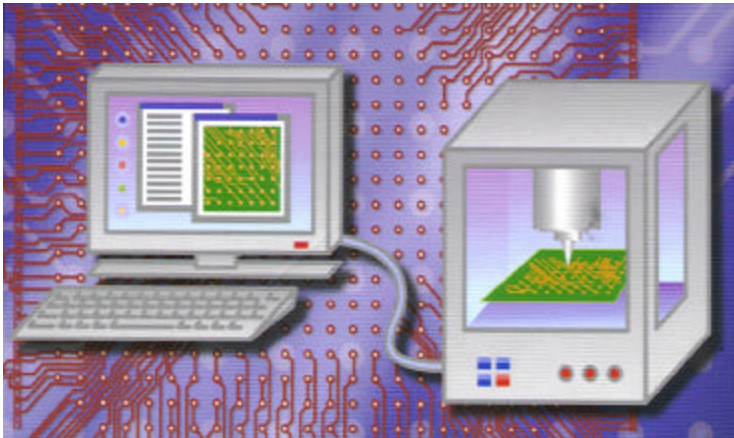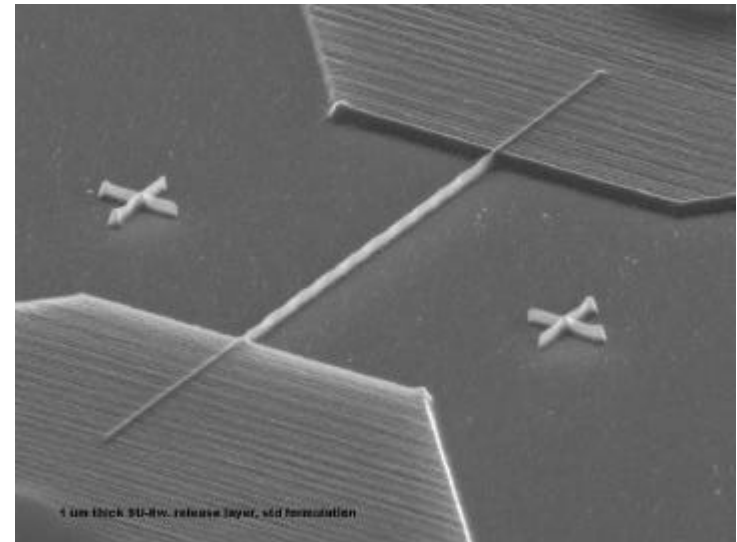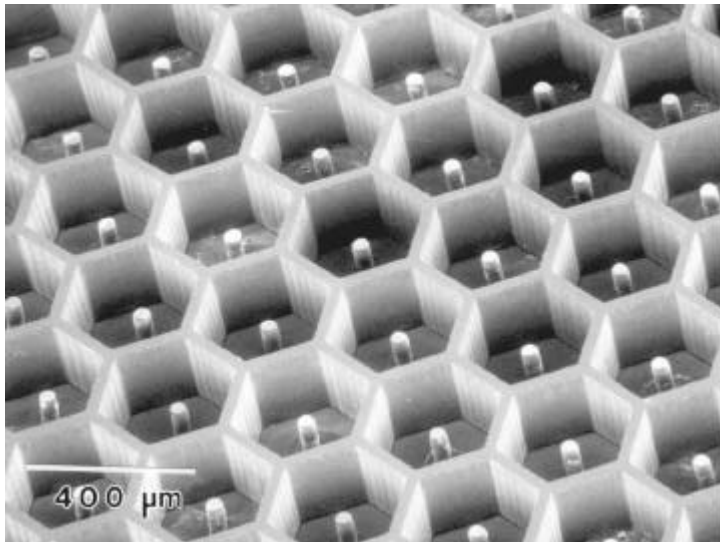
Direct-write Technologies for Rapid Prototyping Applications

Throughput:

Exposure time per "pixel" =

"Sensitivity" / Intensity

Dip-Pen Nanolithography

* as small as 15 nm linewidths and ~ 5 nm spatial resolution
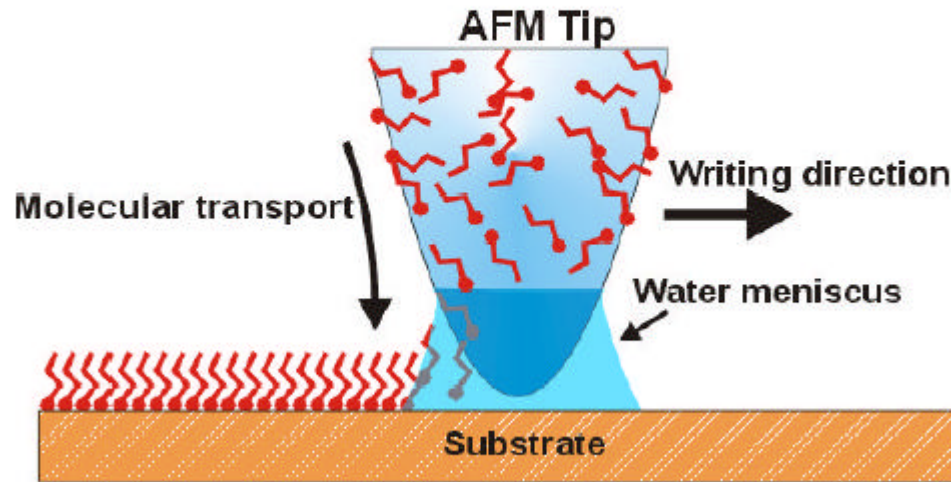
D. Piner, J. Zhu, F. Xu and S. Hong, C. A. Mirkin, "Dip-Pen Nanolithography", Science, 1999, 283, 661-63.

Resolution vs. Areal Throughput (1 sq cm = 10^8 um^2) !

Resolution (angstroms)

STM atom manipulation

Dip pen AFM

E-beam inorganic resist

E-beam PMMA

Shaped e-beam

Optical step & repeat

Areal throughput (um^2 / hr)
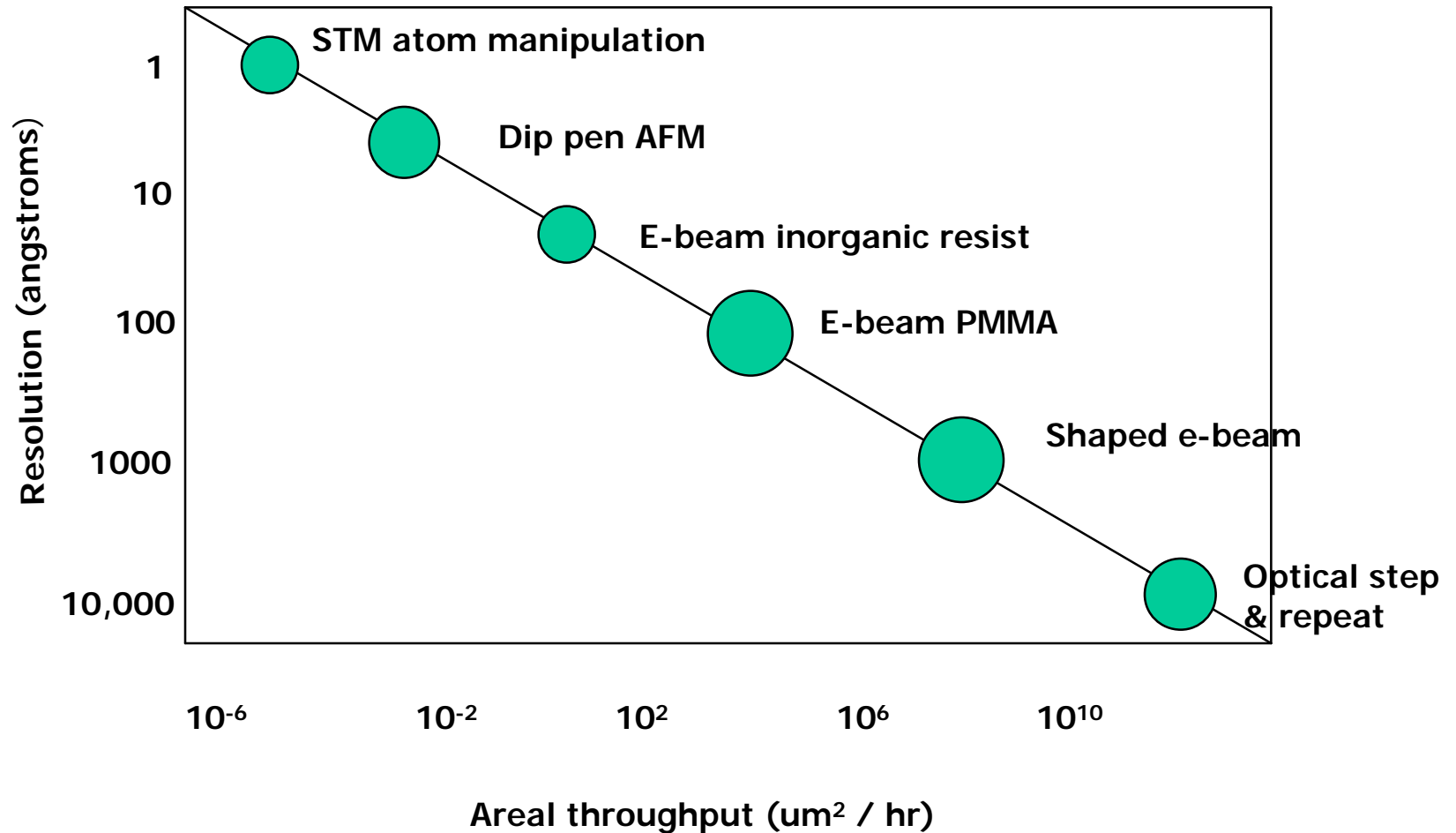
Nanopatterning Lab: Primary Instruments

Sequential Pattern Generation:

High Resolution Electron Beam Pattern Generator (JEOL 9300FS or Leica VB6-HR)
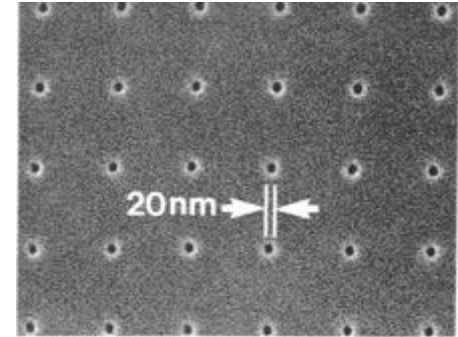
Focused Ion Beam Pattern Generation:

JEOL 9855S with 30 Kv Ga source and high resolution SEM capability for 200 mm wafers
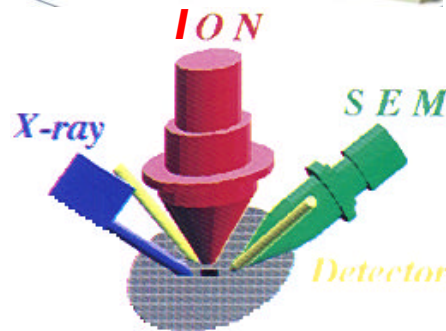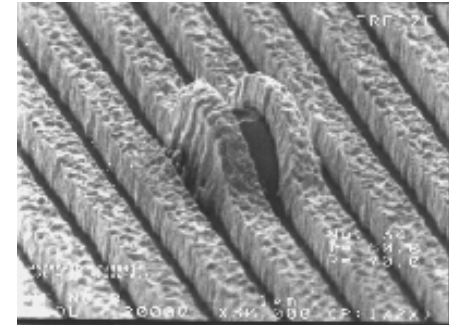
Advantages & Disadvantages of Direct Write Nanofab Methods:

AFM Based   highest resolution, slowest thruput, unproven

Electron Beam   20 nm resolution, medium thruput, proven technology

Ion Beam   100 nm resolution, medium thruput, many substrates (not just resist), Ga ions only!

Laser   lower resolution but reduced cost: no vacuum, no 100 KeV power supplies, etc.

SEM image of patterned hole array in PMMA with silicon substrate patterned by 100 keV JEOL 9300 E-beam pattern generator
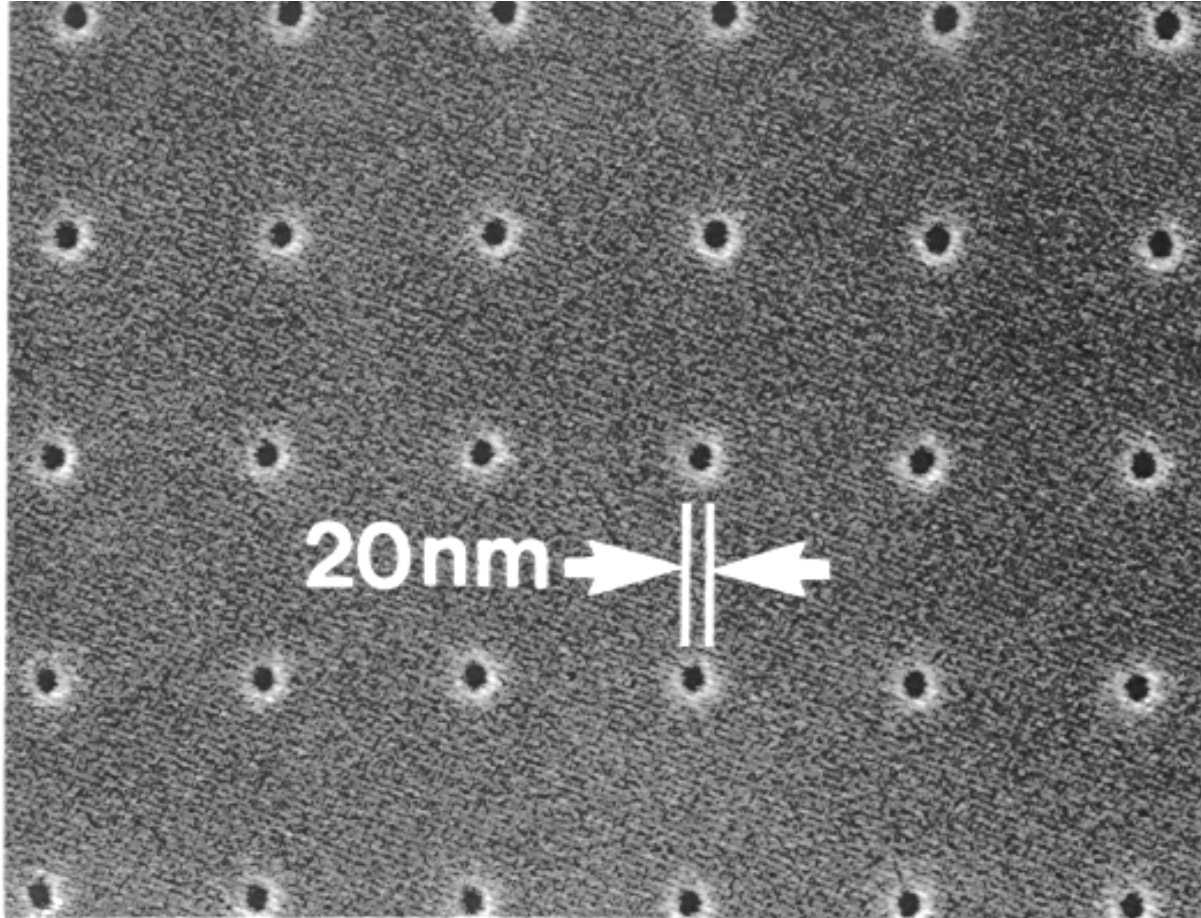
$$l = h / \{2mVe(1 + eV/2mc^2)\}^{1/2}$$

If l = .037 A for 100 keV electrons, why can we pattern (at best) 20 nm dots in PMMA? 20 nm is 5400 greater than l! Yet optical lens's are "diffraction limited" ?
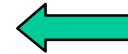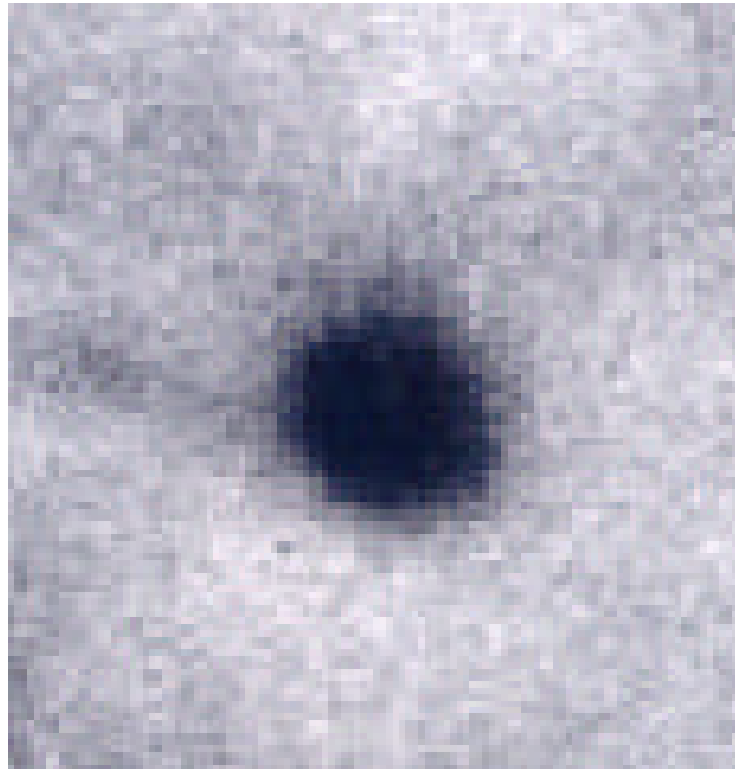
Approx. size of 0.1 nm dot- the resolution of a good TEM, or the STEM in Biology

Fraunhofer diffraction geometry for circular aperture

Assumption of infinite source distance gives plane wave at slit so that all amplitude elements are in phase.

$\tan \Theta = \dfrac{y}{D}$

For distant screen assumption

$\tan \Theta \approx \sin \Theta \approx \Theta \approx \dfrac{y}{D}$

y

a

Θ

Θ'

D

δ For D >> a this approaches a right angle and $\Theta' \approx \Theta$

Condition for minimum
$a \sin \Theta = m \lambda$

$y \approx \dfrac{m \lambda D}{a}$
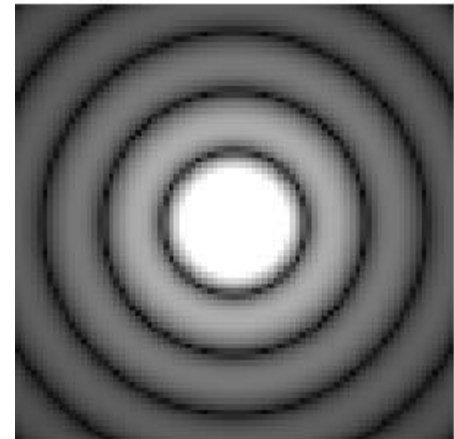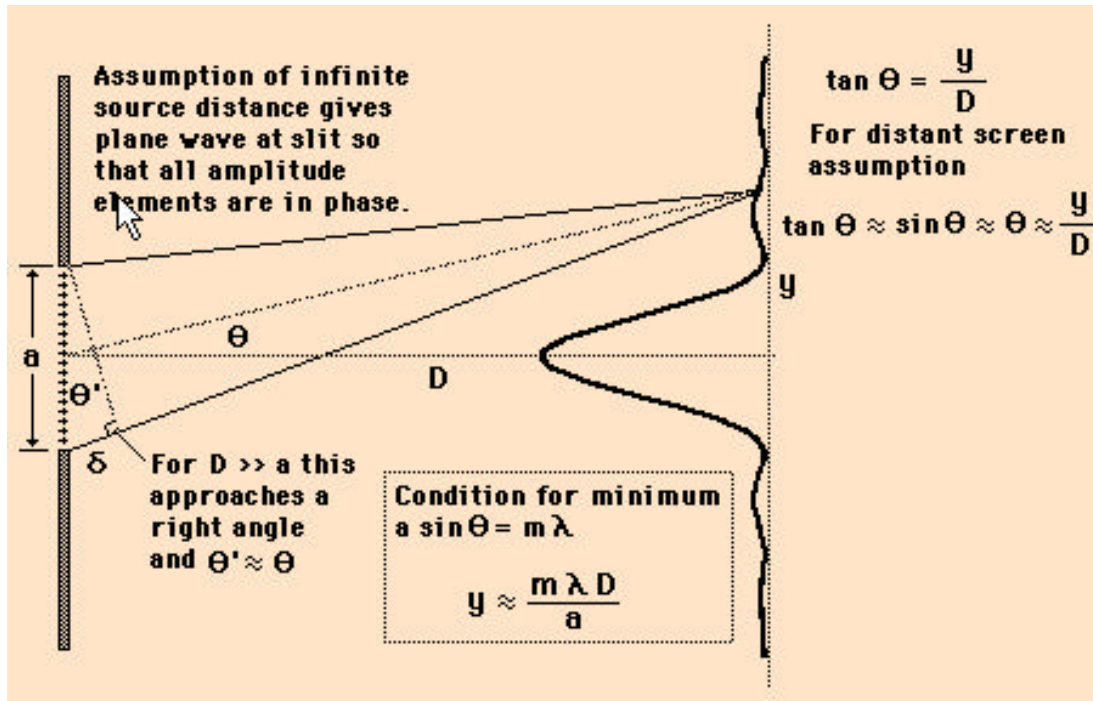
Definition of resolution and spot size

Assumption of infinite source distance gives plane wave at slit so that all amplitude elements are in phase.

For D >> a this approaches a right angle and $\theta' \approx \theta$

Condition for minimum
$a \sin\theta = m\lambda$

$$y \approx \frac{m\lambda D}{a}$$

For the first minimum:

y = λ D / a
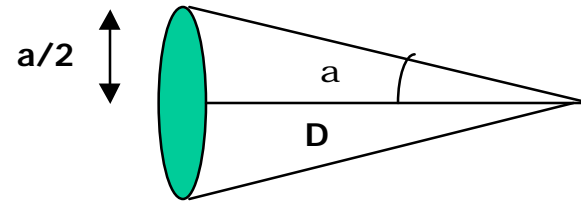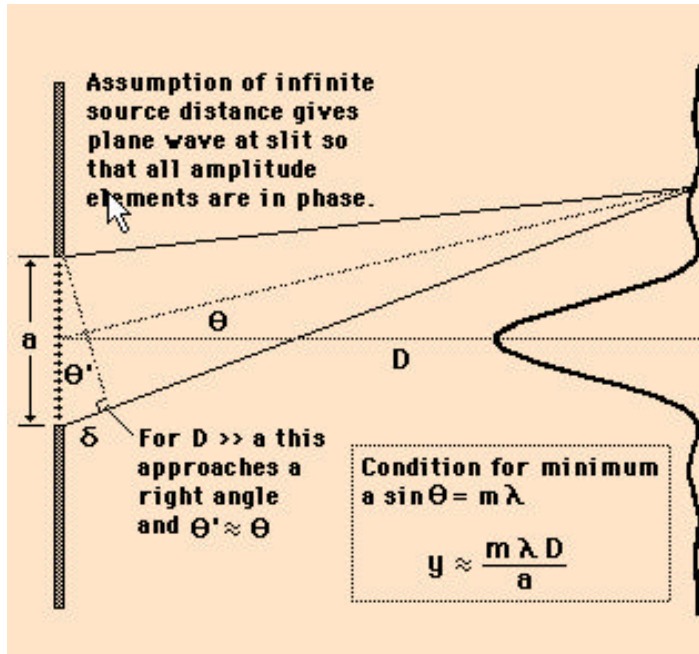
For small angles, a/2 = Dα

Solve for D and substitute:

Or: y = λ / 2 a

So the focused spot diameter is:

        d = 2y = λ / a
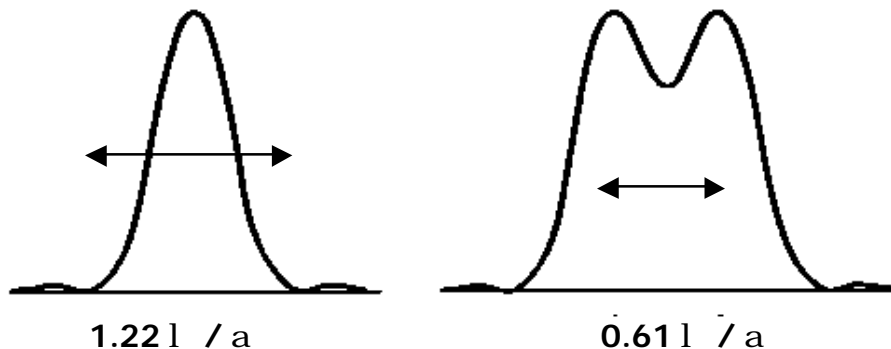
Using the Raleigh resolution criterion:

d = 1.22 λ / a

1.22 λ / a   0.61 λ / a

Spot size as a function of semi-angle:

$$d = 1.22 \, \lambda / \alpha$$

Semi-angle **α**, radians
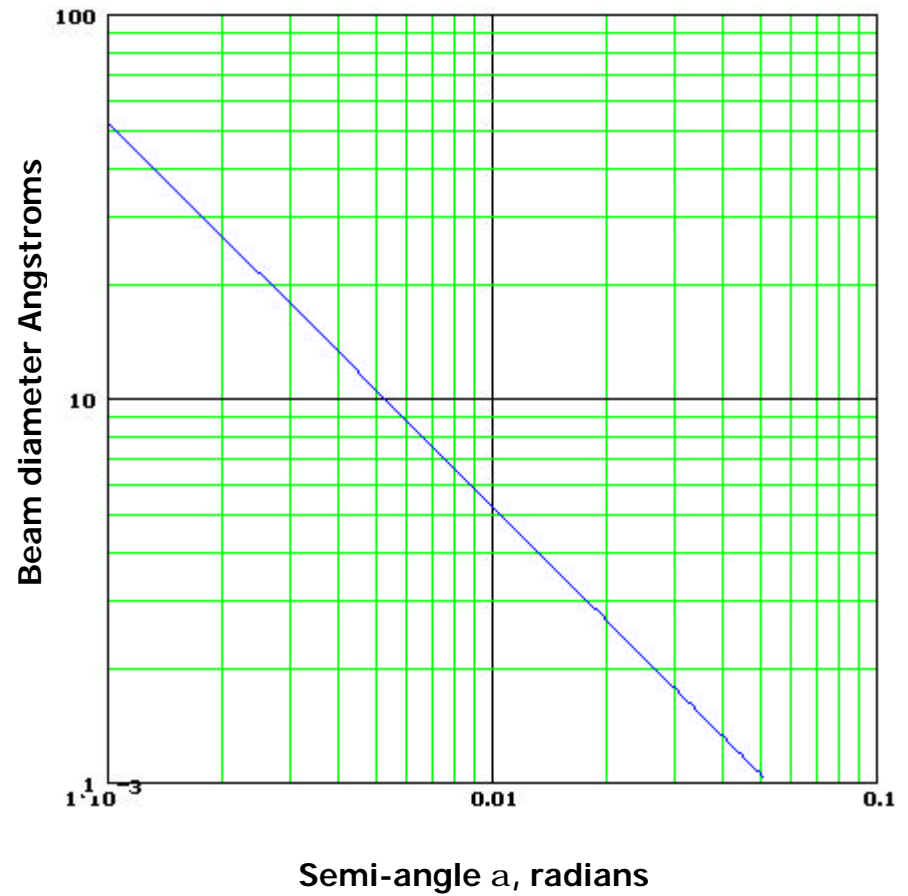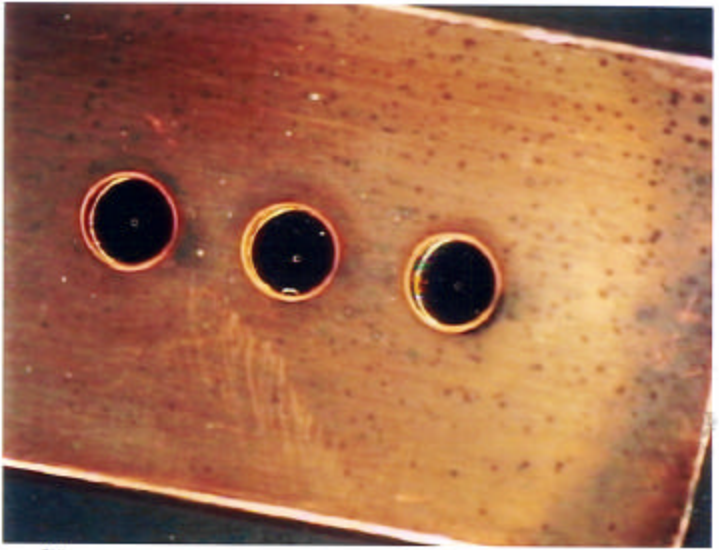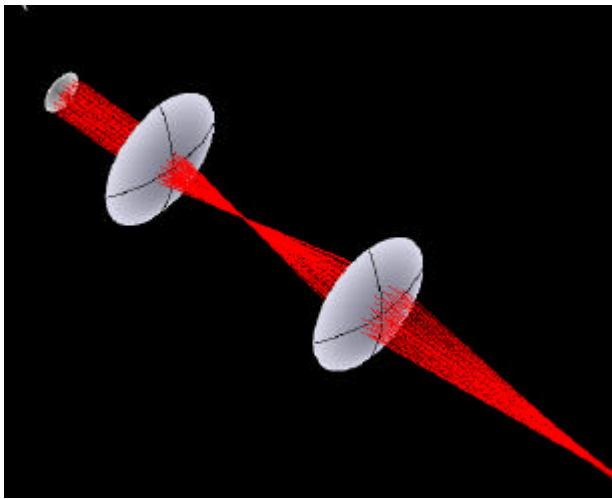
Flux in = Flux out!

(Langmuir theorem for any optical system), so:

b(source) x area x dW = b(image) x area x dW

By definition of a solid angle:

$$dW = p\, r^2 / R^2$$

But $r = Ra$ **for small** a

So $dW = p\, a^2$

Flux = b(source) x area x pa^2

in the image plane.

R

1sr

R

r

a
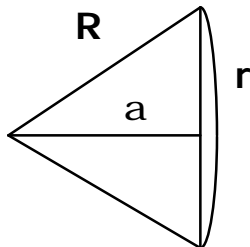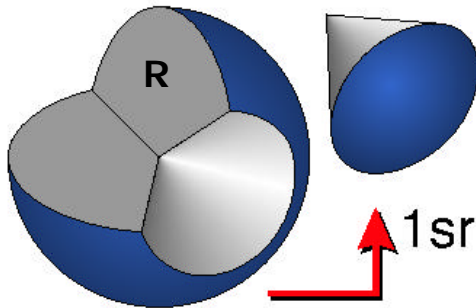
For an electron probe, the flux is replaced by the current I, and the flux expression: b x area x dW becomes:

$$I = b \, (p \, d^2 / 4) \, (p \, a^2)$$

Now we solve for the spot size diameter:

$$d_g = (2 \, I^{1/2} / p \, b) \, (1 / a)$$

and we have defined the probe size using geometrical rather than physical optics

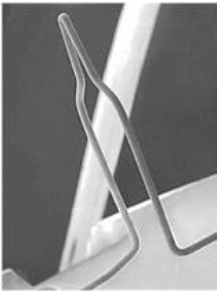# Electron beam probe size based on diffraction and geometrical optics considerations for a 100 keV electron gun

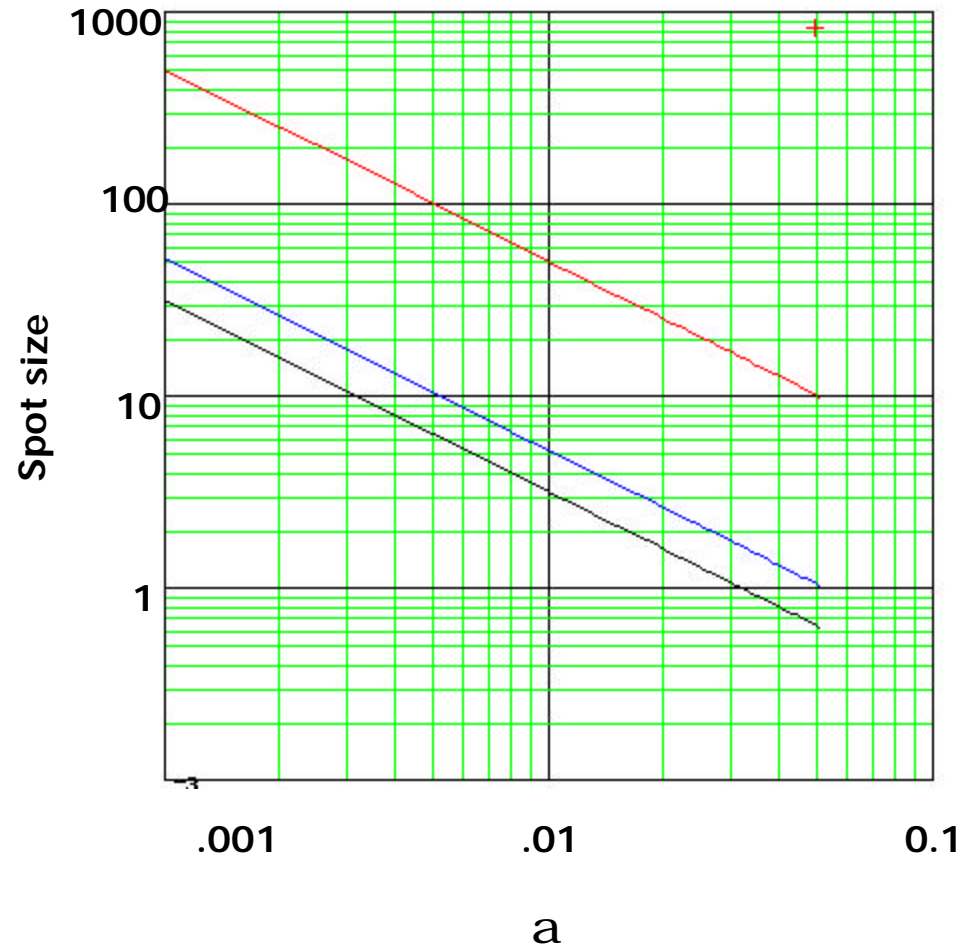**W thermal emission:**
$b = 1 \times 10^{-11}$ **amps / sq. Angstrom**

Field emission:

$b = 2 \times 10^{-8}$ **amps / sq. Angstrom**

Spot size (y-axis): 1000, 100, 10, 1

a (x-axis): .001, .01, 0.1

$$d = 1.22\, l / a \qquad d_g = (2\, l^{1/2}/p\, b)\,(1 / a)$$

E field for focusing electrostatic lens and sample electron trajectories
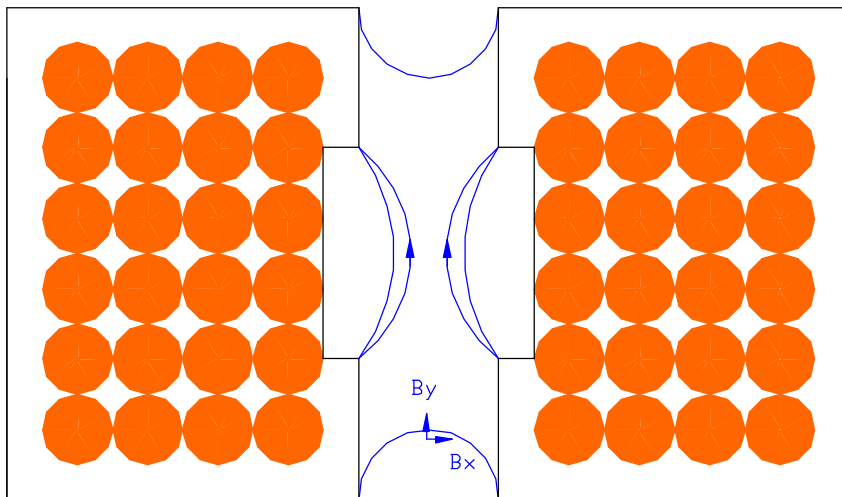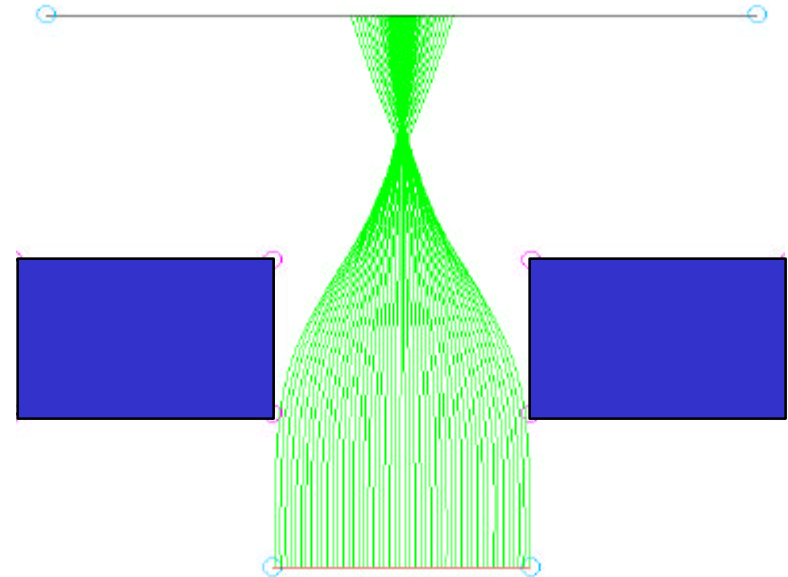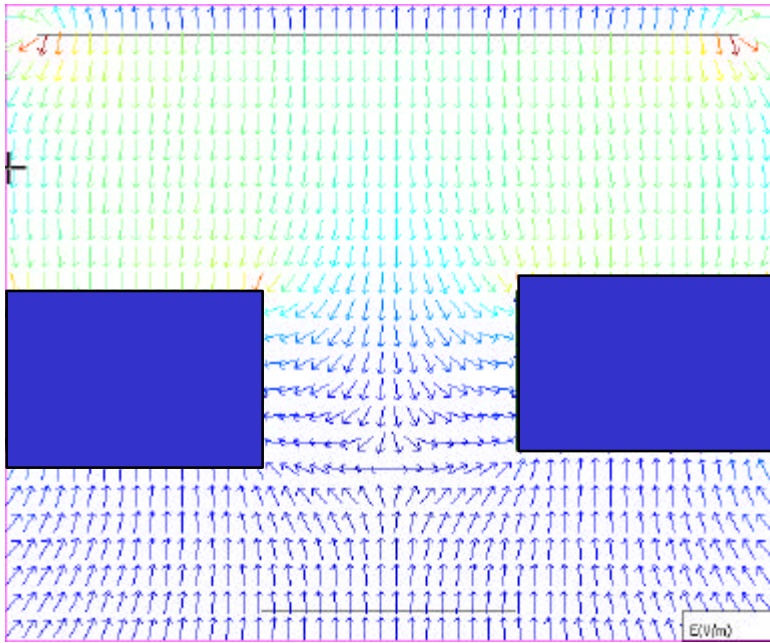
Electromagnetic lens

$$F = q(E + v \times B)$$

Spherical aberration for electrostatic lens - external rays are brought to focus at shorter distance than paraxial rays

$$d_s = C_s a^3$$
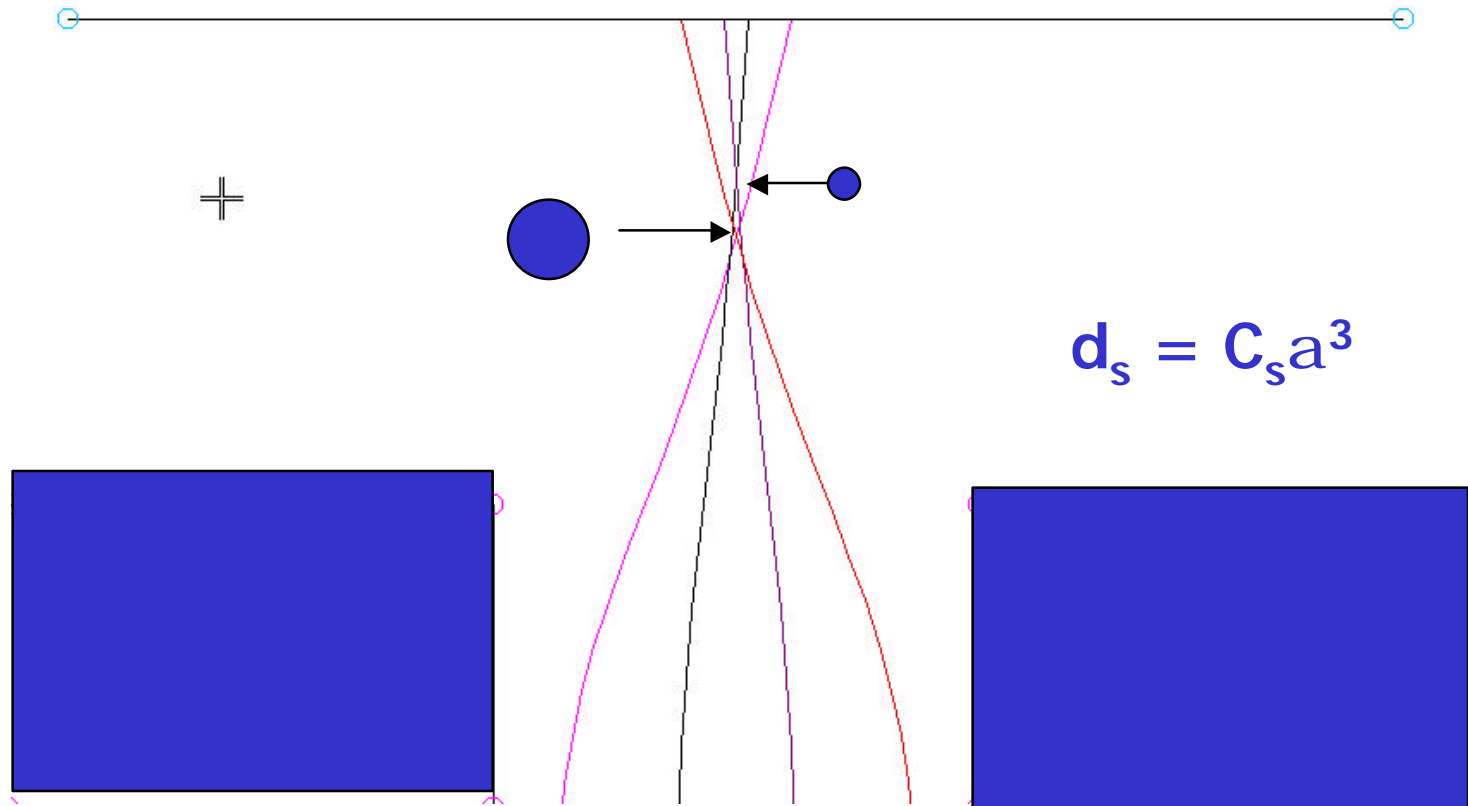
Chromatic aberration for electrostatic lens - less energetic electrons are brought to focus in shorter distance than ones with high energy

6 keV

4 keV

$$d_c = C_c\, a\, dE / E$$

Summing the contributions for diffraction, brightness, spherical aberration and chromatic aberration, we have:

$$d_i := 0.61 \cdot \frac{\lambda}{\alpha_i}$$

$$dgf_i := \left(\frac{2}{\pi} \cdot \sqrt{\frac{I}{\beta}}\right) \cdot \frac{1}{\alpha_i}$$
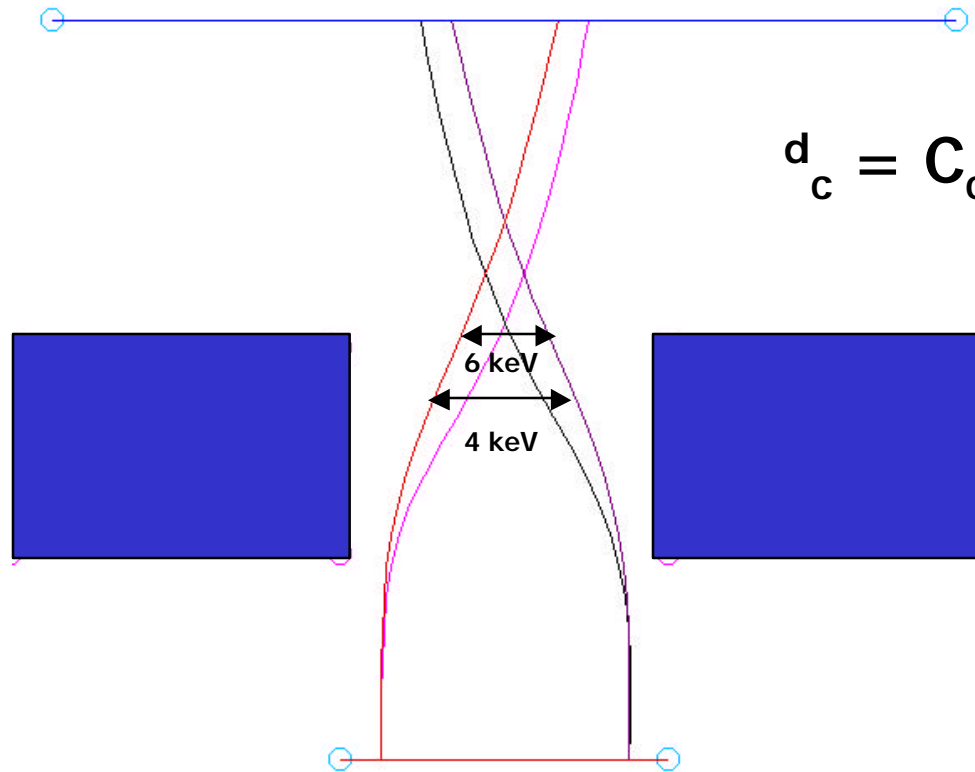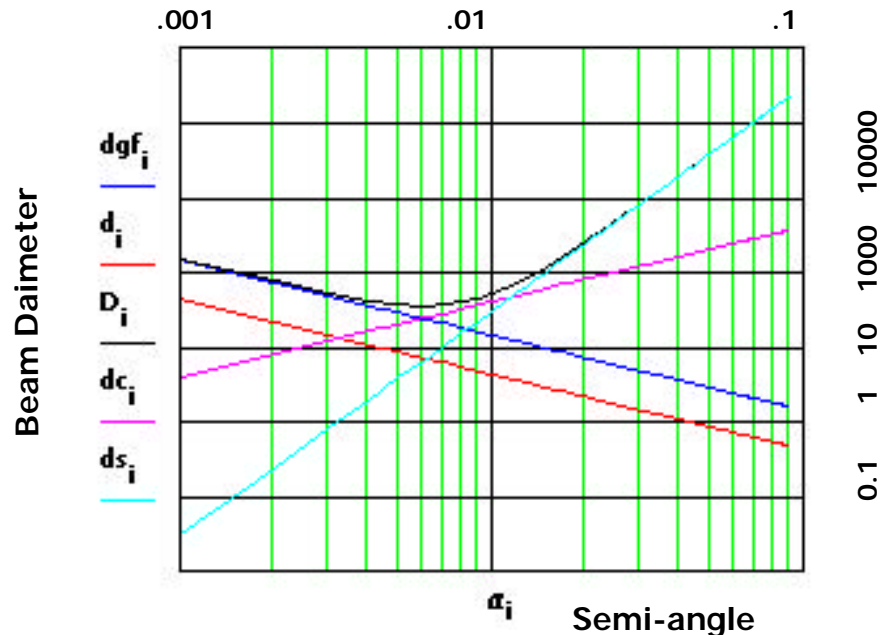
$$dc_i := Cc \cdot \alpha_i \cdot \frac{\delta E}{E}$$

$$ds_i := .30 \cdot Cs \cdot \left(\alpha_i\right)^3$$

$$D_i := \sqrt{\left(d_i\right)^2 + \left(dgf_i\right)^2 + \left(ds_i\right)^2 + \left(dc_i\right)^2}$$

The *area's* are summed to get total spot size:

Spherical aberration

+

Chromatic aberration

+

Gaussian

+

Diffraction

Beam Daimeter

dgf_i

d_i

D_i

dc_i

ds_i

.001   .01   .1

10000   1000   10   1   0.1
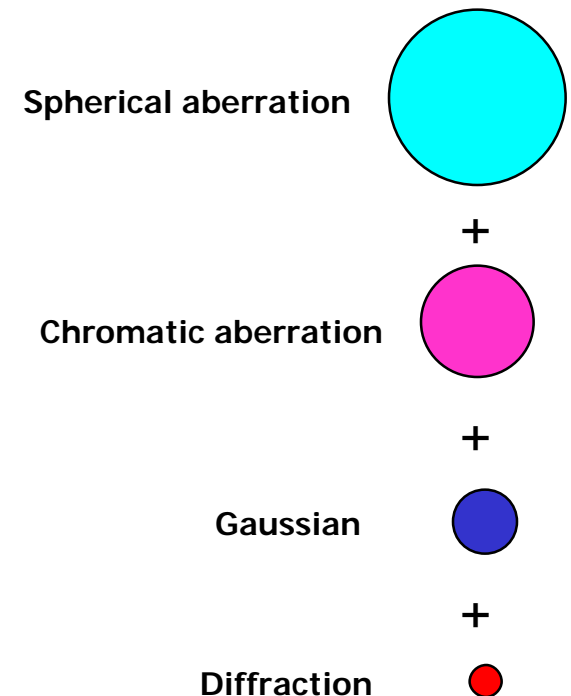
α_i **Semi-angle**

Beam diameter as a function of semi-angle for high and low accelerating voltage
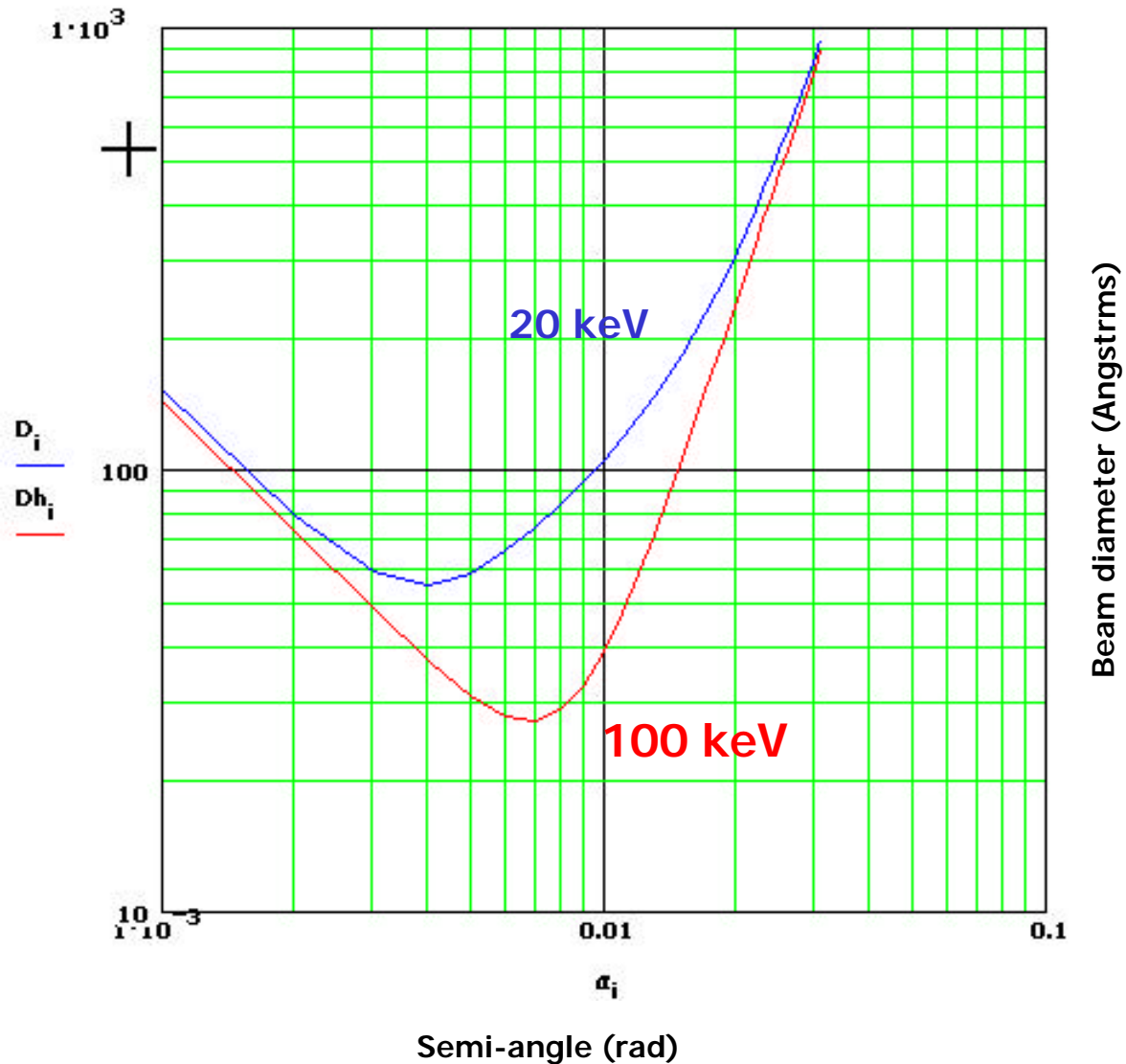
Electron beam diameter as a function of gun brightness
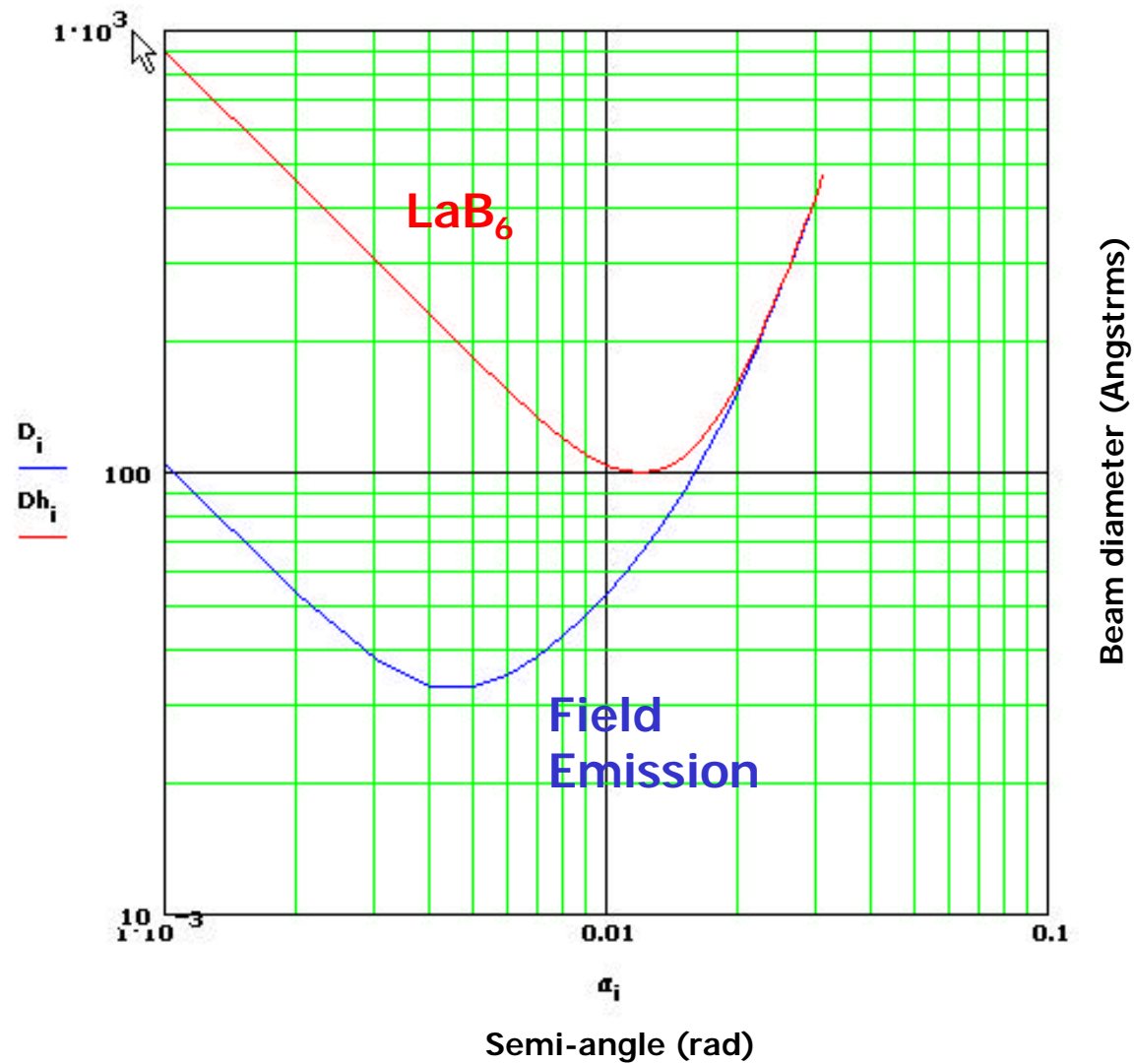
Probe diameter as a function of current for a fixed semi-angle:

Probe Current in Amperes
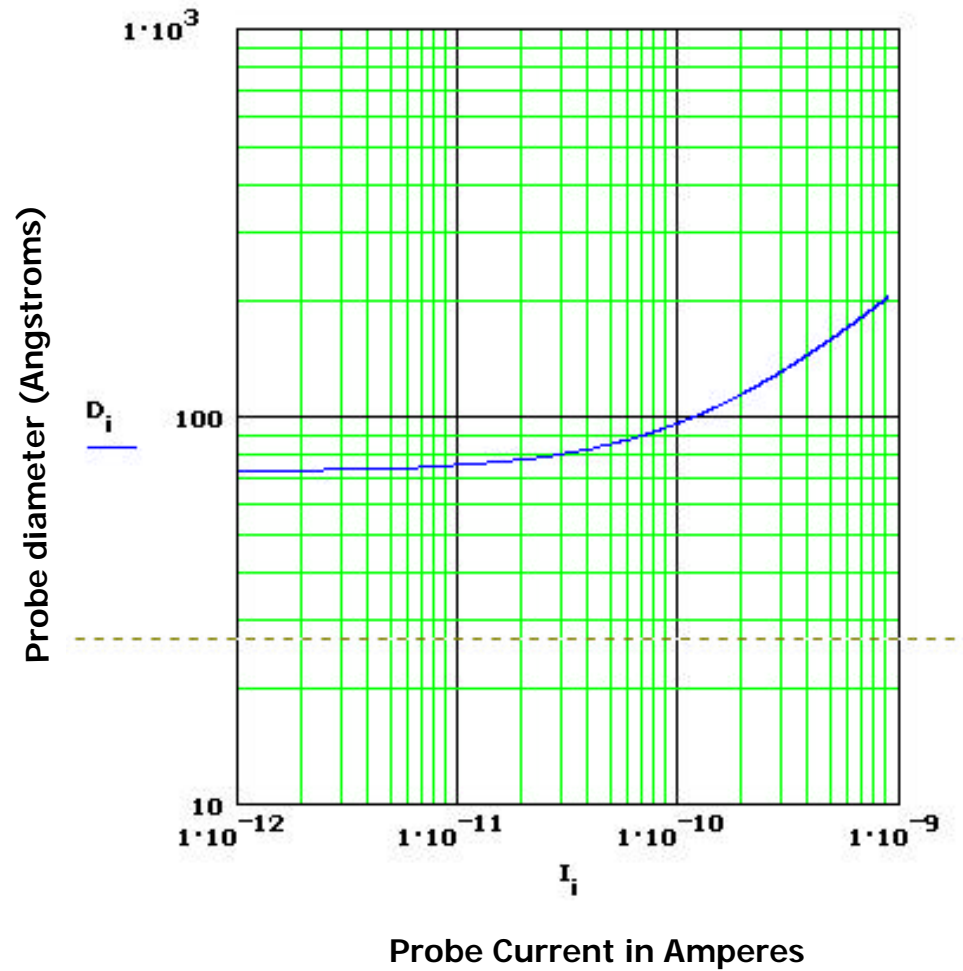
Why is it so difficult to eliminate spherical aberration for both electrostatic and electromagnetic lens's?
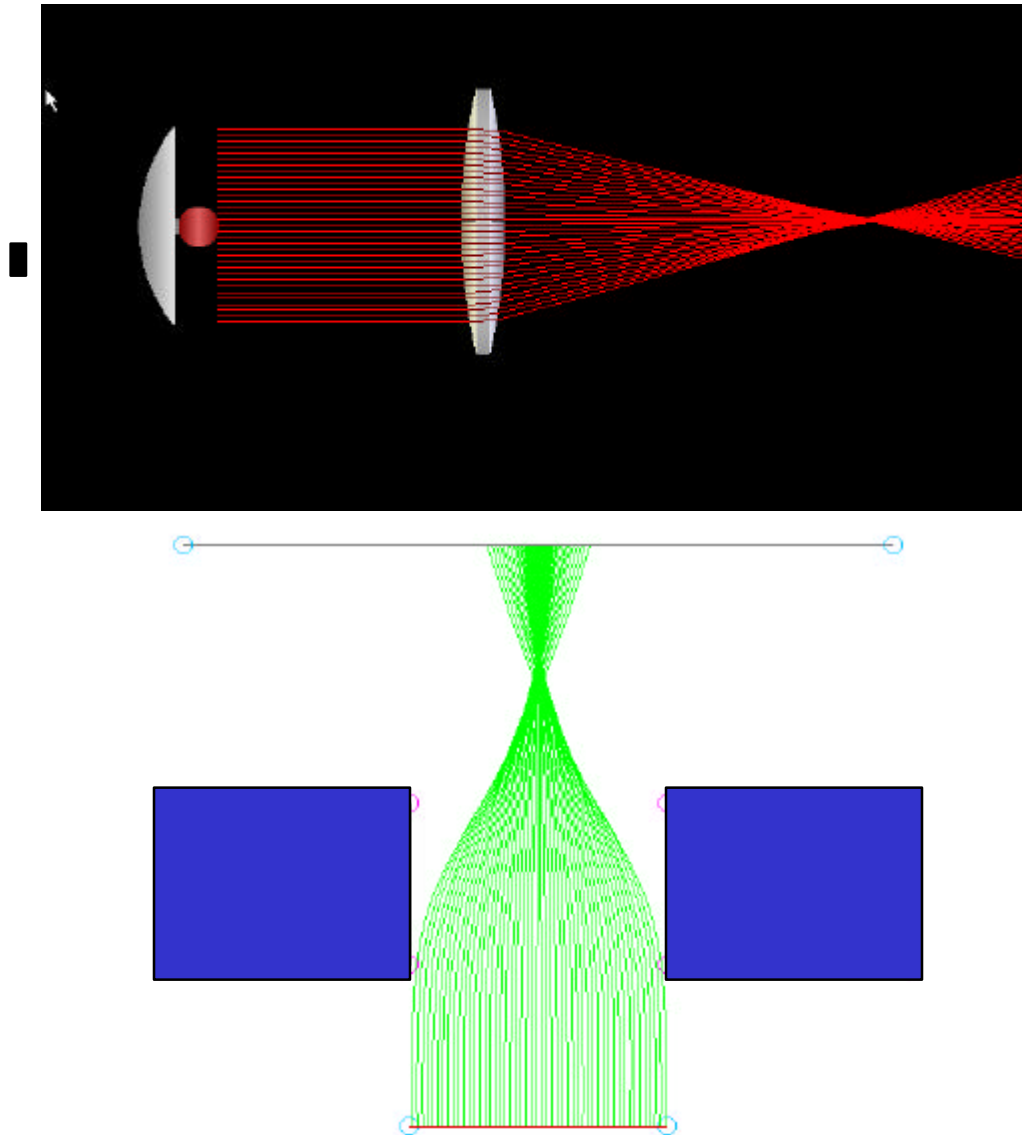
Sub-nanometer spot size's are obtainable for field emission-based instruments, but the minimum feature size in resist is still much larger. WHY?
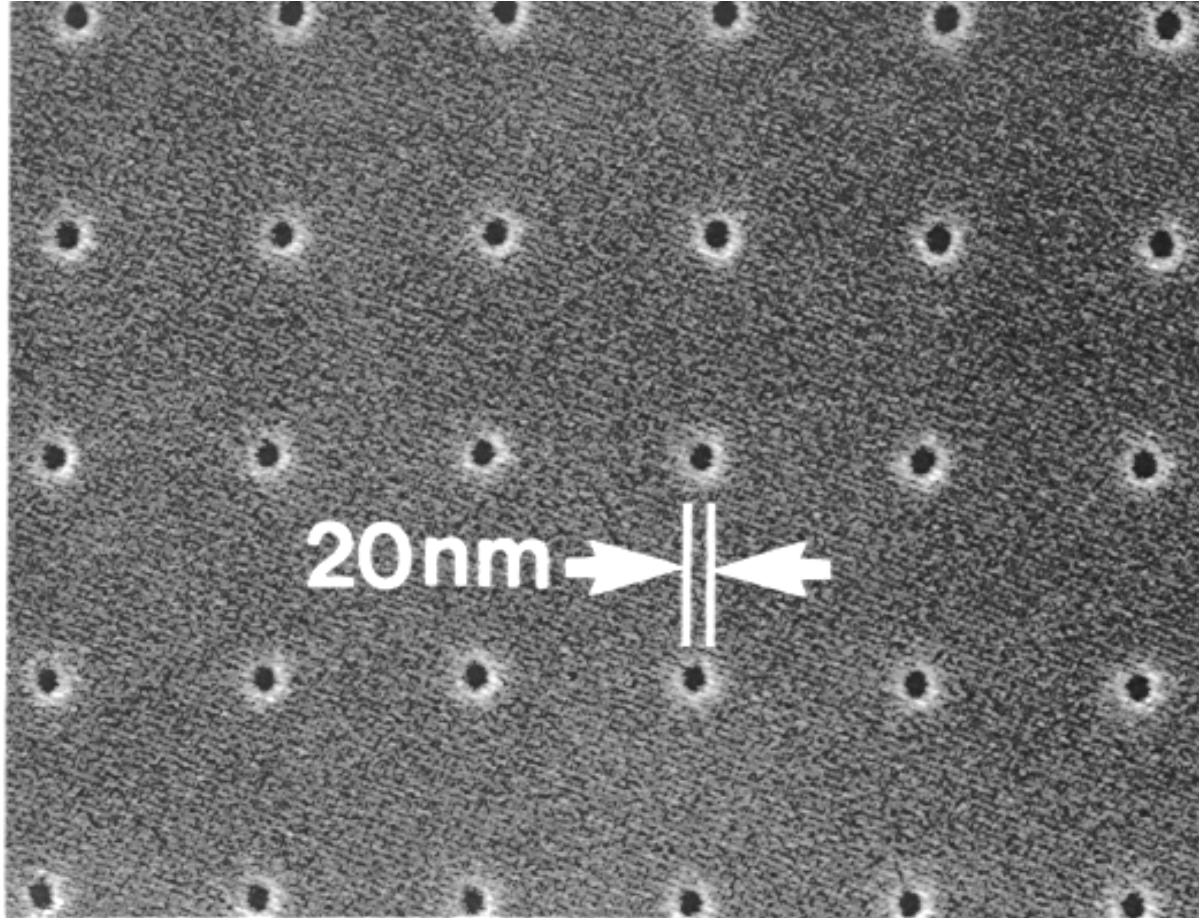
Electron-matter interactions:

Electron beam

Secondary Electrons (nm range)

Auger electrons

Backscattered electrons (10's of nm to 100 nm

Continuous X-rays

Fluorescent X-rays

Characteristic X-rays (um range)
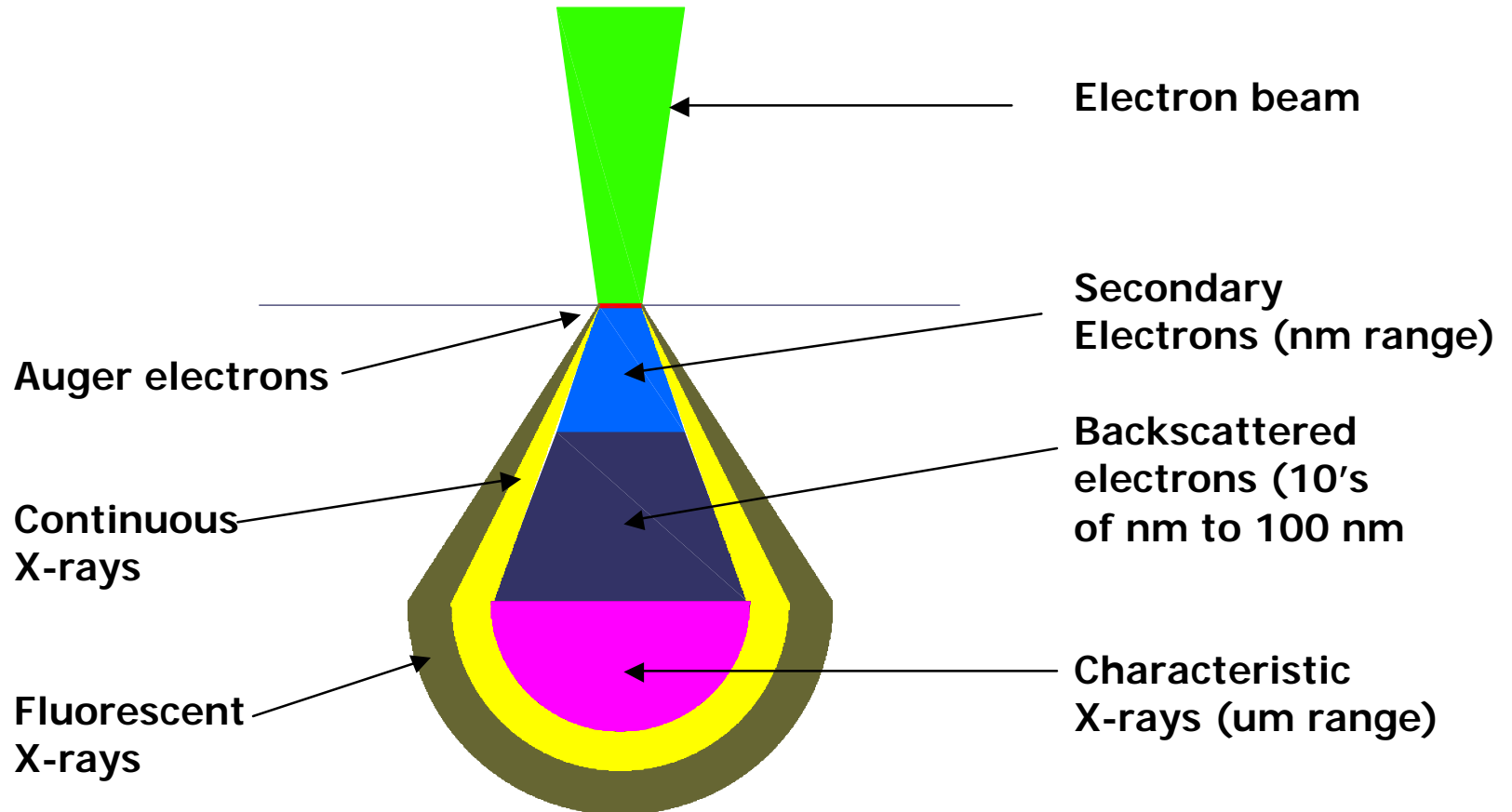
Assumptions for Monte Carlo electron scattering:

1) Elastic (no energy loss) scattering (attraction between electron and nucleus; repulsion between electron and electron cloud resulting in angular path deviations) *completely determines the path taken by the electron.*
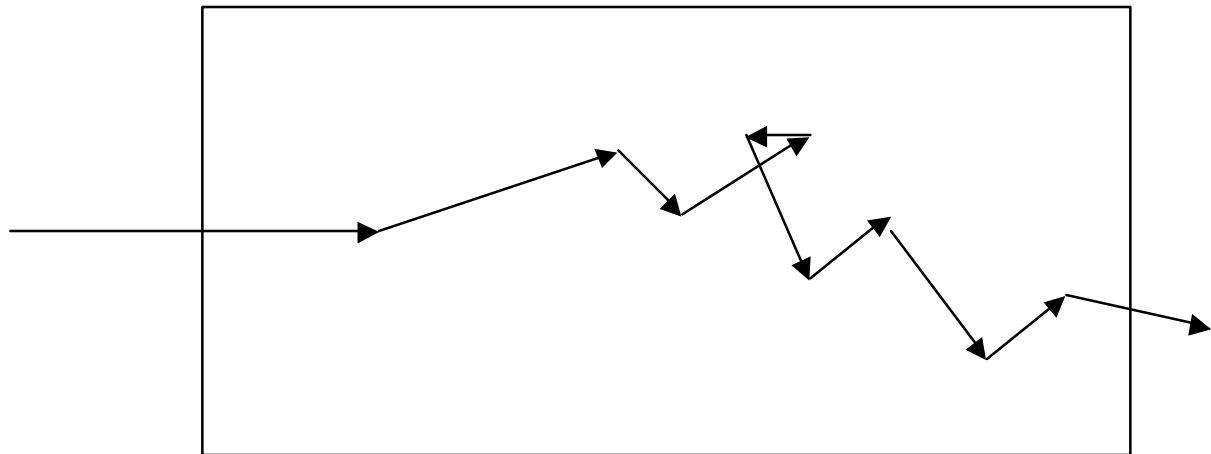
2) Inelastic scattering (energy loss) *takes place continuously along the path followed by the electron rather by discrete events* (inner shell ionization, etc)

3) Actual atom positions are ignored; matter is treated as a continuum.

The average distance traveled by the electron between elastic scattering events, is l, the mean free path:

$$l = A / N_a r \, s_E$$

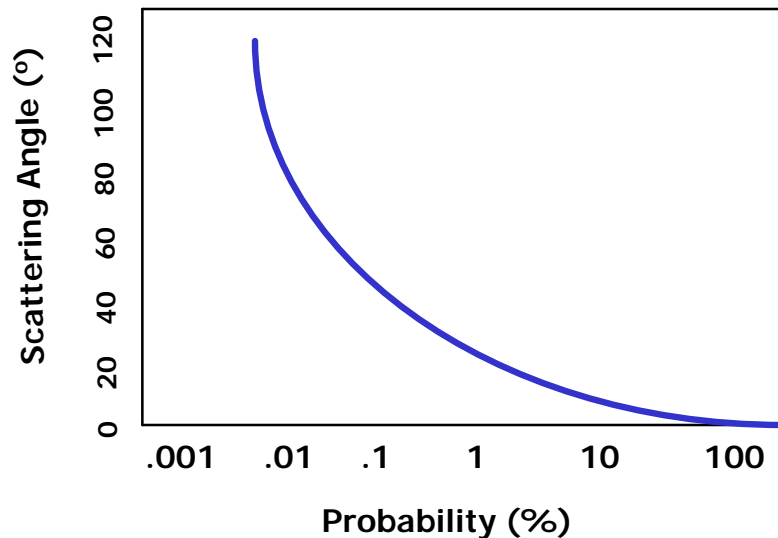l **as a function of electron energy and atomic number:**

Element	Z	100 keV	10 keV
Carbon	6	1310 A	170 A
Silicon	14	1112 A	127 A
Copper	29	297 A	35 A
Gold	79	89 A	10 A

In the Monte Carlo simulation, a random number generator determines the step length and the scattering angle for the electron path.
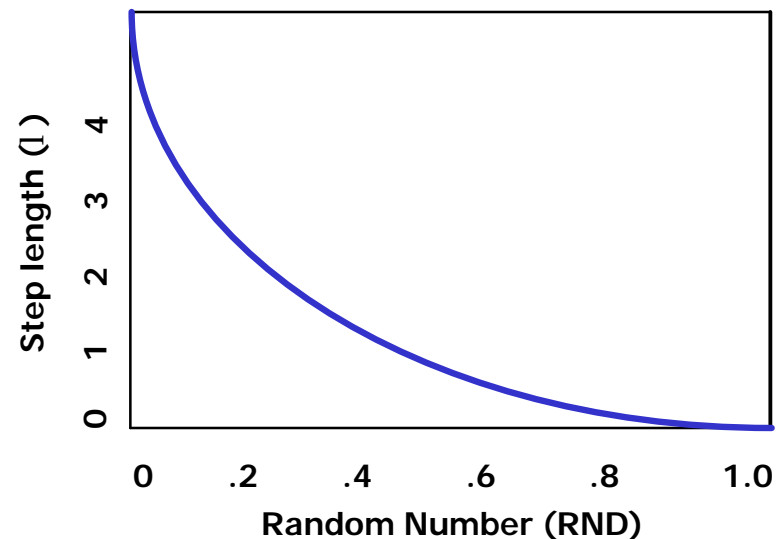
$$\text{Cos } \pmb{f} = 1 - \frac{2 \, \pmb{a} \text{ RND}}{(1 + \pmb{a} - \text{RND})}$$

$$y = 2 \pmb{p} \text{ RND}$$

Probability of scattering angle exceeding a specified value. Most angles are small, but 50 % > 1.5⁰

The average step length is $\pmb{l}$, but s is > 2.3 $\pmb{l}$ 10% of the time.

Scattering Angle (°) vs Probability (%)

Step length ($\pmb{l}$) vs Random Number (RND)

Program sequence:*

1. Find the step length for a given material and energy.

$s = -\mathbf{l} \ln (RND)$

2. Find the angular deviation in terms of the direction cosines:

$\mathbf{f} = \cos^{-1} (2 \, \mathbf{a} \, RND / 1 + \mathbf{a} - RND)$

$\mathbf{y} = 2 \, \mathbf{p} \, RND$

where $\mathbf{a}$ is a function of the energy and atomic number.

3. Use a form of the "Bethe stopping power" eqn to compute energy lost:

$dE/dS = -78500 * (Z/AE) \ln (1.166E / J)$

where $S = \mathbf{r}s$ and J is the mean ionization potential.

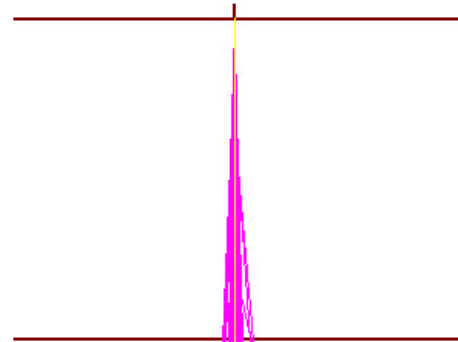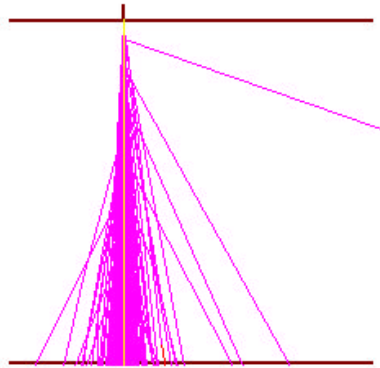4. Using the direction cosines, compute the new position: xyz and assign the new energy to the electron.

*courtesy D. C. Joy, Oak Ridge Nat'l Lab
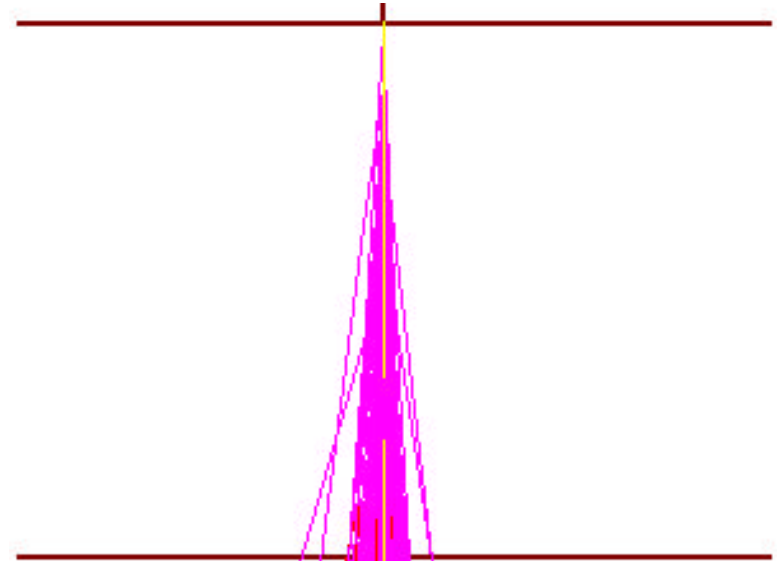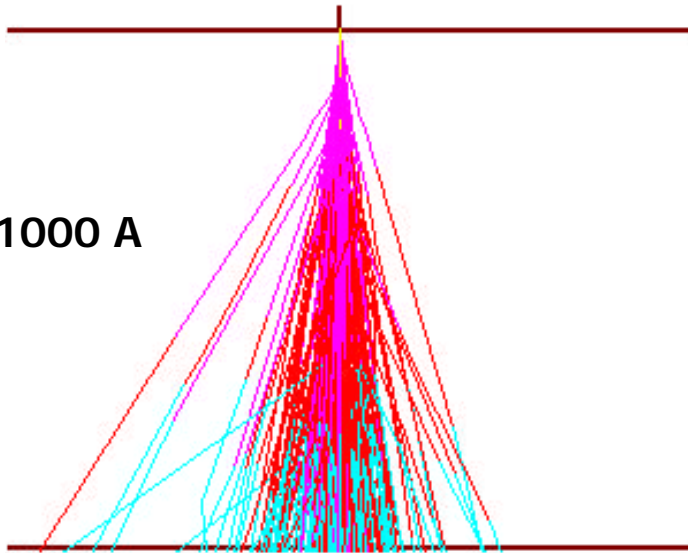
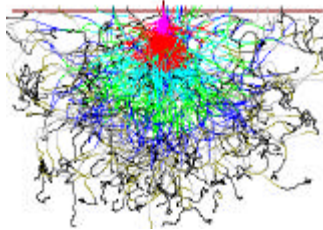# Scattering simulation in PMMA membranes
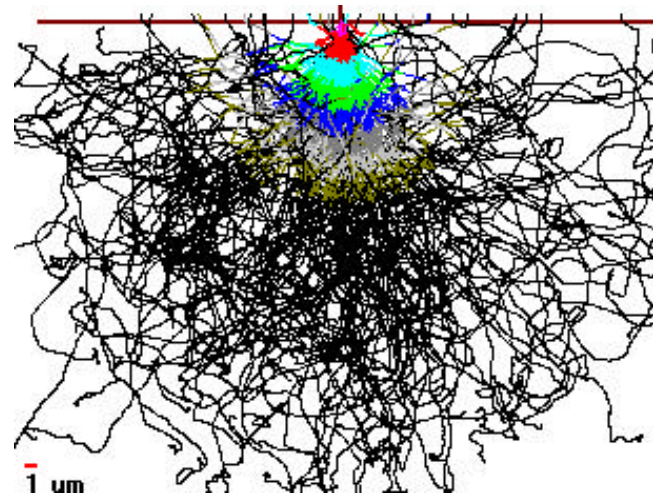

25 keV

100 keV

500 A

1000 A

Simimulation of scattering of 25 keV and 100 keV electrons in bulk silicon substrate:
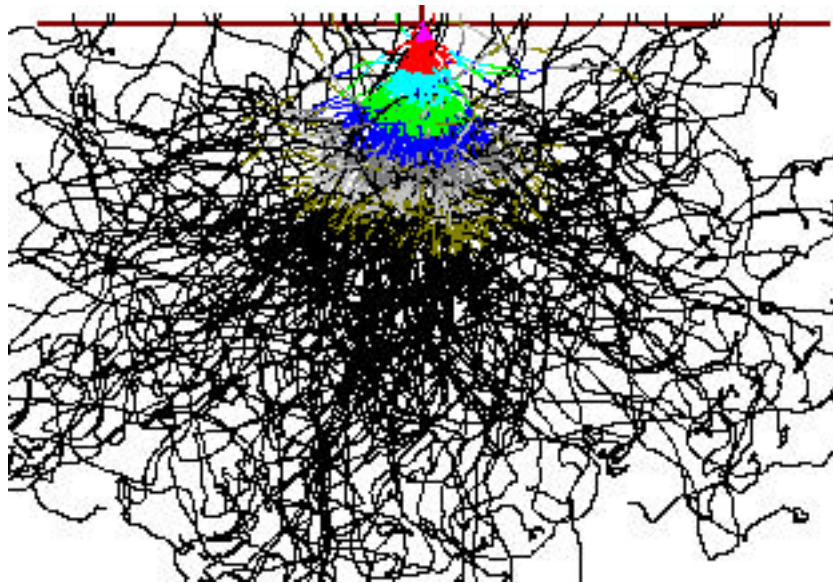
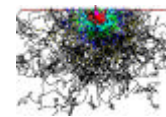**25 keV**   **100 keV**

1 µm

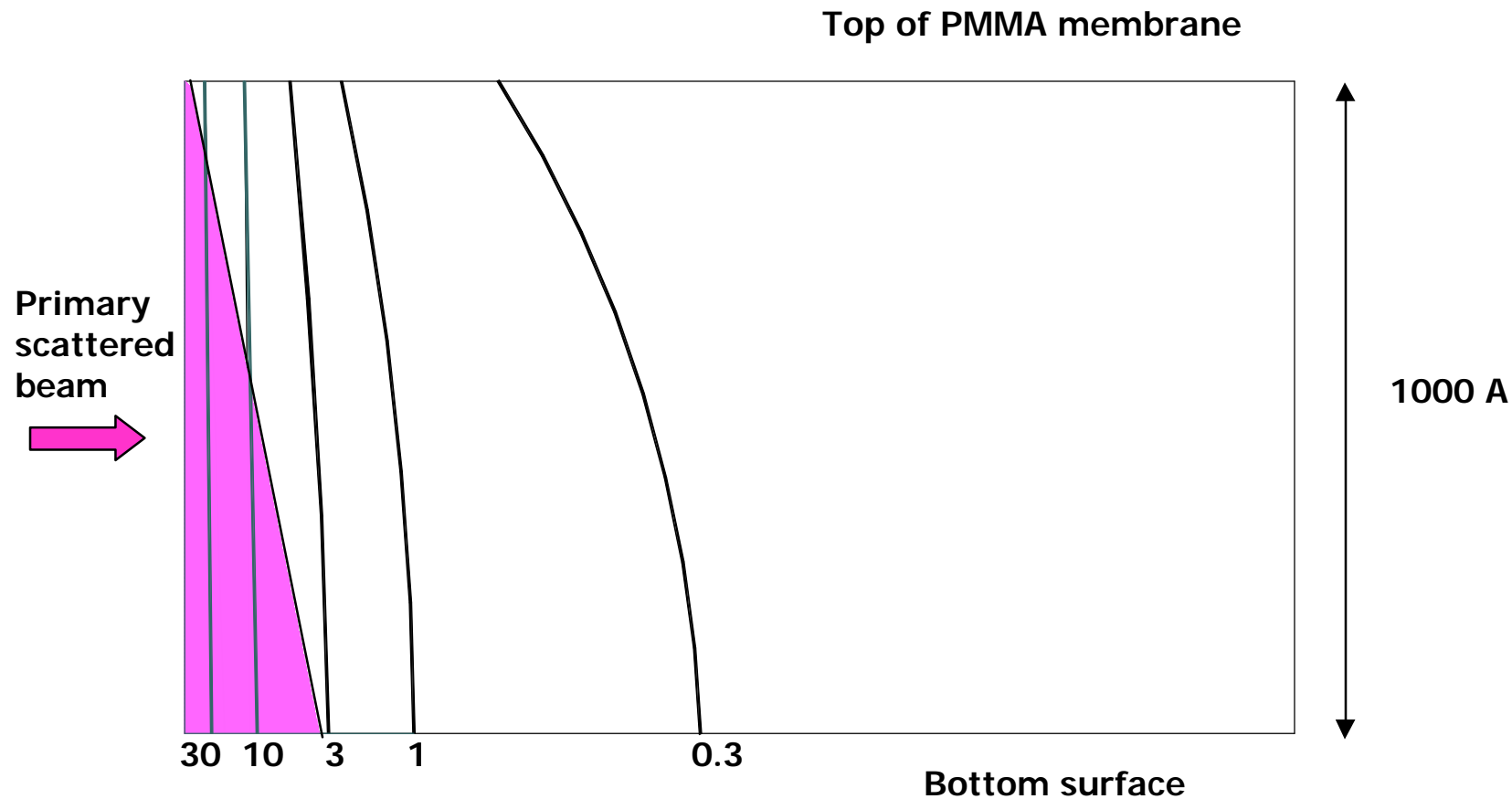# Simulation of 100 keV electrons with low Z and high Z elements

Silicon

Tungsten

Energy contours in 1000 A PMMA film exposed by 100 keV electron beam

Top of PMMA membrane

Primary scattered beam

1000 A

30   10   3   1   0.3

Bottom surface

Summary:

1) The "limits" of resolution for any electron probe system are determined as much by electron-substrate interactions as the optics.
2) Electron-resist and electron-substrate interactions must be optimized as we approach genuine nanoscale geometries.
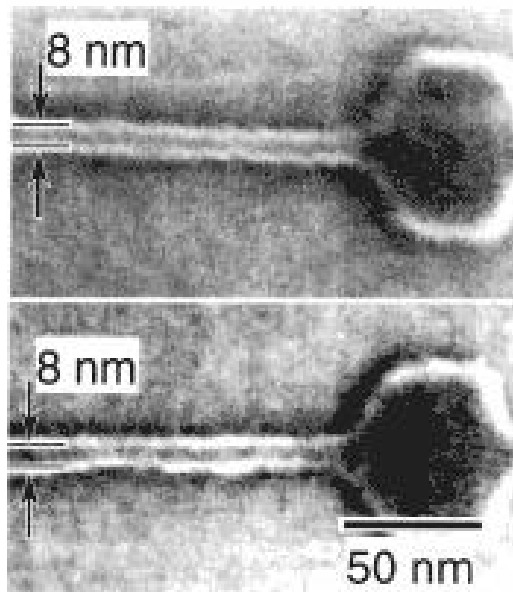
1   **2**

1. Sub-10 nm Electron Beam Lithography using Inorgainc Resist, K. Yamamzaki et al. Proc. SPIE 3997 (2000) 458.
2. Univ. of Glasgow, unpublished rept.